



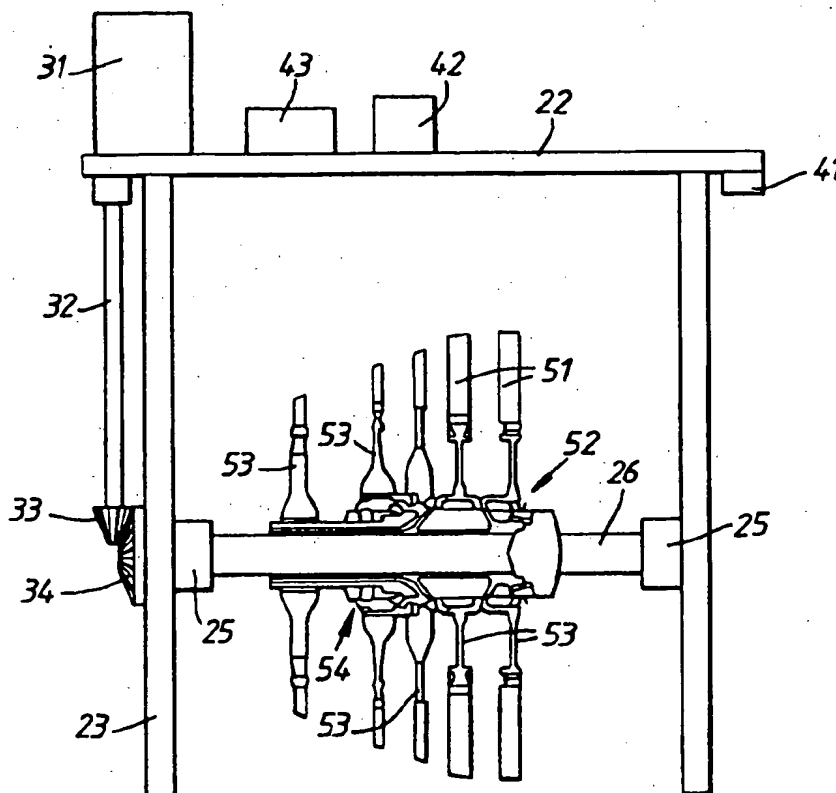
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/GB94/00374 (22) International Filing Date: 25 February 1994 (25.02.94) (30) Priority Data: 9303853.7 25 February 1993 (25.02.93) GB (71) Applicant (for all designated States except US): BAJ COAT-INGS LIMITED [GB/GB]; Banwell, Weston-super-Mare, Avon BS24 8PD (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): FOSTER, John [GB/GB]; 3 Vian End, Worle, Weston-super-Mare, Avon BS22 9QD (GB). TAYLOR, Alan [GB/GB]; 2 Bilbie Road, Worle, Weston-super-Mare, Avon BS22 0QE (GB). CHATTERLEY, Martin, Patrick [GB/GB]; 5 Powys Close, Milton, Weston-super-Mare, Avon BS22 9AG (GB). (74) Agents: ROBINSON, Anthony, John, Metcalf et al.; Kilburn & Strode, 30 John Street, London WC1N 2DD (GB).		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>

(54) Title: METHOD OF PRODUCING AN ABRASIVE TIP ON A TURBINE BLADE

(57) Abstract

A method of producing abrasive tips on compressor or turbine rotor blades by electrolytic or electroless deposition in which at least part of the deposition process is conducted on the blades assembled on a compressor or turbine rotor disc. The tips are therefore formed on the blades after they are put into their final operating positions on the disc so that subsequent disassembly which has hitherto been necessary is avoided. The assembly is preferably mounted with its rotational axis horizontal and deposition may be accompanied by vibration of the assembly in the vertical direction.



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METHOD OF PRODUCING AN ABRASIVE TIP ON A TURBINE BLADE

This invention relates to blades for turbines and compressors and in particular relates to the production of blade tip seals.

It is known to provide at the tip of a gas turbine blade a tip portion comprising abrasive particles which are embedded in a matrix, the tip being intended to run against the surface of a shroud of a material which is softer than the abrasive particles. By this means, it is possible to produce, by the abrasive action of the particles on the shroud, a gap between the tip and the shroud which is very small, thus minimising gas losses. In one particular example where this technique is used, the matrix comprises a major part of cobalt and minor parts of chromium, tantalum and alumina while the lining material of the shroud comprises a major part of cobalt with minor parts of nickel, chromium and aluminium and a small quantity of yttrium. Various methods for producing such tips have been proposed. In one example, detonation spray coating of the matrix is used. In another example there is first produced an inner tip portion of mainly nickel and cobalt with additional ingredients by casting as a single crystal and the inner tip portion is, after shaping, diffusion bonded to the tip of the blade body. The abrasive portion of the tip is then formed on the inner tip portion by electrodeposition of alternating layers of chromium and nickel about the abrasive particles. The outer tip portion can then be aluminided to produce a matrix alloy of NiCrAl.

There has been described in GB-A-2241506 a method of producing a gas turbine blade having an abrasive tip which comprises producing a binding coat on the tip of the blade body by electrodeposition, the binding coat

comprising MCrAlY where M is one or more of iron, nickel and cobalt, anchoring to the binding coat coarse particles of an abrasive material by composite electrodeposition from a bath of plating solution having the abrasive particles suspended therein, and then plating an infill around the abrasive particles. It has been found that this method, all stages of which are of a metal plating nature and are therefore relatively inexpensive and readily controllable, produces a very effective abrasive blade tip.

All the methods for producing blades with tip seals are expensive and time consuming and it is an object of the present invention to provide a method of producing blades with tip seals which is cheaper and more satisfactory than the prior methods referred to.

According to the present invention, compressor or turbine rotor blades are assembled on a compressor or rotor disc and abrasive tips are produced on the tips of the assembled blades by electrodeposition or by electroless deposition.

Production of the tips on the assembled blades has several advantages, the chief of which is that it is possible to carry out various production steps on the assembled disc without subsequent disassembly. The present practise is for the blades to be assembled on the disc and for the blade tips to be machined to produce a properly balanced disc. The blades are then marked, disassembled from the disc, mounted on a jig, tipped, removed from the jig and then reassembled on the disc in the same order and positions that they previously occupied. By proceeding in accordance with the invention, one of the two assembly operations, jiggling and dejiggling, the marking and the disassembly are avoided and unbalancing due to the blades being re-

assembled in slightly different attitudes or positions from those previously adopted is obviated.

5 The process according to the invention is particularly suited to blade tipping using the methods described in GB-A-2241506 in which a binding coat is produced on the tip of each blade by electrodeposition, coarse particles of an abrasive material are anchored to be binding coat by composite electrodeposition of the particles and an anchoring coat and then plating an
10 infill around the particles. The binding coat may comprise MCrAlY where M is one or more of iron, nickel and cobalt. The anchoring coat may be of cobalt or nickel or MCrAlY as defined above and the infill may also be MCrAlY and defined above.

15 The blades are tipped while assembled on a compressor or rotor disc, which term is intended to cover bosses, rings and similar blade mounting elements which terms are used for substantially the same structures. Although it is possible to treat the discs individually,
20 further benefits can be obtained by first assembling a plurality of rings together to form a part or a whole turbine or compressor rotor. This again reduces the steps required and helps to maintain balance.

Various particles may be employed. Examples include
25 zirconia, alumina and various nitrides, silicides and borides known from the abrasive art. The preferred abrasive is cubic boron nitride, preferably having a particle size between 125 and 150 μm . It is possible for the infill, or at least the upper or outer portion
30 thereof, to include abrasive particles of a size substantially smaller than the main abrasive particles, for example approximately 20 μm .

The MCrAlY of the binding coat, the anchoring layer where this is MCrAlY, and the infill where this is MCrAlY

may have various compositions of which suitable examples are described in British Patent Specification GB-2167446B. The electrodeposition may be effected by various forms of apparatus. However, suitable forms of apparatus are described in British Patent Specification Nos. GB-2182055A and European Patent Specification No. EP-0355051A. These describe apparatus which comprises an electroplating tank which is divided into two zones by a vertical wall extending from close to the bottom of the tank up to just beneath the surface of the solution in the bath. Gas is admitted to one of the zones to induce an upward flow of solution therein, the solution, with particles entrained therein, spilling over the weir formed by the upper edge of the division wall and descending in the second zone in which the article to be coated is located. The latter specification describes rotating the article with a stop-start or quick-slow cycle.

Where the infill is of MCrAlY, that is it consists of particles of CrAlY in a metal matrix, the deposition of the infill is preferably accompanied by vibration of the assembly, preferably in a vertical direction. It is believed that such vibration ensures an even distribution of CrAlY particles, particularly in those regions which are shaded by the overhang of the abrasive particles and which regions might otherwise be depleted of particles. The frequency of the vibration is preferably between 10 Hz and 1 kHz, the particularly preferred figure being about 50 Hz. A peak acceleration of up to 10 g is preferred. It is believed that a particularly good result is achieved by vibrating at two alternating levels, for example a vibration with a peak level of about 2 g alternating with a vibration with a peak level of about 10 g. Preferably, each lower level phase is

longer than each higher level phase; thus the lower level phases may be for between 30 seconds and 2 minutes duration with a peak acceleration of about 2 g and the higher level phases may be for about 5 seconds duration with a peak acceleration of about 10 g.

The invention may be carried into practice in various ways but a process of producing a gas turbine blade in accordance with the invention together with apparatus suitable for carrying out the process will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is a perspective view of one of the plating baths used in the process;

Figure 2 is a side elevation of the apparatus shown in Figure 1;

Figure 3 is a front elevation of the apparatus shown in Figure 1;

Figure 4 is a perspective view of a fixture used in the apparatus shown in Figures 1 to 3;

Figure 5 is a front view of the fixture shown in Figure 4 with an assembly mounted thereon; and

Figure 6 is an enlarged section through part of the tip region of a blade having an abrasive tip produced in the manner to be described.

The process to be described is intended to form abrasive tips on the blades of a gas turbine rotor assembly 52 which is shown in Figure 5. The assembly comprises five turbine discs 53 mounted on a hollow shaft assembly 54 forming part of the complete turbine. The shaft assembly is mounted on a shaft 26 for the tipping process which will be described below. Each of the discs 53 has mountings, for example fir-tree slots, in which the roots of the blades are mounted. It should be emphasised that in the preferred procedure the blades are

mounted in the discs in their final positions and will not subsequently be disassembled from the discs.

5 The tipping process is carried out in the apparatus shown in Figures 1 to 3 of the drawings. This comprises a vessel or container 1 having a parallelepiped shaped upper portion 2 and a downwardly tapering lower portion 3 in the form of an inverted pyramid which is skewed so that one side face 4 forms a continuation of one side face 5 of the upper portion.

10 The vessel 1 contains a partition 6 which lies in a vertical plane parallel to the side faces 4 and 5 of the vessel and makes contact at its side edges 7 and 8 with the adjacent vertical and sloping faces of the vessel. The partition thus divides the vessel into a larger working zone 9 and a smaller return zone 11. At its 15 bottom the partition 6 terminates at a horizontal edge 12 above the bottom of the vessel to afford an interconnection 13 between the working zone 9 and the return zone 11. At its top, the partition 6 terminates at a horizontal edge 14 below the top edges of the vessel 1. 20

At the bottom of the return zone 11 there is an air inlet 15 which is connected to an air pump (not shown). Mounted in the working zone 9 is a fixture 21 to which 25 the assembly to be coated is mounted, the fixture 21 being arranged to position the assembly within the vessel in a manner to be described in greater detail below. Conductors, not shown, are provided to apply a voltage to the assembly mounted on the fixture 21 relative to an anode which is suspended in the working zone. 30

To use the apparatus to codeposit a coating on the blade tips of the assembly, the assembly is mounted on the fixture 21 which is positioned in the vessel as shown. Before or after the positioning of the fixture,

the vessel is filled to a level 17 above the top edge 14 of the partition 6 with a plating solution containing particles to be co-deposited. Air is admitted to the inlet 15 and this rises up and the return zone 11, raising solution and entrained particles. At the top of the return zone. The air escapes and the solution and particles flow over the broad crested weir formed by the top edge 14 of the partition and flow down past the assembly on the fixture 21. At the bottom of the working zone 9, the particles tend to settle and slide down the inclined sides of the vessel towards the interconnection 13 where they are again entrained in the solution and carried round again.

As the downwardly travelling particles in the working zone 9 encounter the tips of the blades at the top of the assembly, they tend to settle on the these tips where they become embedded in the metal which is being simultaneously plated out.

The fixture 21 on which the workpieces to be coated are mounted is shown in detail in Figures 4 and 5, in simplified form in Figures 2 and 3 and is omitted from Figure 1 for reasons of clarity. The fixture 21 comprises a deck 22 which fits over the top of the vessel 1, a depending pillar 23 towards one end and a depending pillar 24 at the other end, the pillars having journals 25 in which the ends of the shaft 26 of the assembly are mounted. The deck 22 supports an electric motor 31 which rotates the shaft 26 through chain wheels 27,28 and a chain 29.

At each end of the underside of the deck 22 there are springs 41 by which the jig is supported on the edges of the vessel 1 as seen in Figures 2 and 3. Mounted on the deck 22 is a vibrator 42 whose operation can be adjusted as required by a controller, not shown. An

electronic motor controller 43 is mounted on the deck 22 and is connected by lines 45 to the motor 31. The controller 43 is designed so that the motor 31 is driven in one direction only so as to rotate the shaft 26 about a horizontal axis.

The use of apparatus of the construction described to produce abrasive tips on the gas turbine blades will now be described.

The assembly 52 is degreased in a vapour degreaser or a proprietary degreasing agent such as GENKLENE (Registered Trade Mark). The assembly is then grit blasted as necessary to provide a key for the masking wax and the assembly is then inserted into a wax bath to mask all the surfaces of the discs and blades. The assembly is then mounted in journals and rotated so that the tips of the blades move past a wiper which removes the masking wax from the tips of the blades. The assembly is then given an anodic clean for five minutes at 6 to 8 volts in a cleaning solution consisting of sodium hydroxide/gluconate/thiocyanate and is then rinsed thoroughly in cold running water. The exposed tips of the blades are then etched by submerging the assembly in a solution comprising approximately 300 gms/l ferric chloride, 58 gms/l hydrochloric acid and 1% hydrofluoric acid (60% w/w) for five minutes at room temperature and again rinsed thoroughly in cold running water. The assembly is then placed in a nickel chloride bath to provide a strike which is given at 3.87 amps per square decimeter (36 amps per square foot) for four minutes. The strike bath comprises approximately 350 gms/l nickel chloride and 33 gms/l hydrochloric acid.

The assembly is then placed in the fixture shown in Figure 4 and the fixture is placed in the apparatus shown in Figures 1 to 3. The bath contains a cobalt plating

5 solution with 20 to 30 weight percent particles of CrAlY containing 67-68 parts by weight Cr, 29-31 parts by weight Al and 1.5 to 2.4 parts by weight Y with a size distribution both in the bath and in the as-deposited coating as given in the following table, the columns relating to the size band being the upper and lower limits of the cut measured in micrometers.

Table

	Size Band		Per Cent
10	118.4	54.9	0
	54.9	33.7	0
	33.7	23.7	0.3
	23.7	17.7	1.3
	17.7	13.6	4.3
15	13.6	10.5	17.7
	10.5	8.2	38.1
	8.2	6.4	18.3
	6.4	5.0	12.3
	5.0	3.9	8.2
20	3.9	3.0	0.1
	3.0	2.4	0
	2.4	1.9	

25 Plating is continued for a period of 4 hours at a current density of 0.075 amps per decimeter (10 amps per square foot) with the controller set to rotate the motor at such a speed as to rotate the assembly at 0.33 revolutions per minute. Air is admitted continuously to maintain circulation of the solution and suspended CrAlY particles. This plating provides a binding coat of CoCrAlY on the tips of the blades to a thickness of between 25 and 50 μm . Deposition of CoCrAlY from the bath described will produce a layer having a composition which is approximately in weight percent: Al 10, Cr32, Y

30

0.5 and the balance Co.

The assembly is then rinsed over the tank with demineralised water and then removed from the region of the tank and rinsed in running water. The holder is then placed in a Woods nickel bath or 1 volume percent sulphuric acid bath to reactivate the surfaces and the assembly is then placed in a second bath similar to the first bath except that in place of the CrAlY particles it contains particles of cubic boron nitride of 100/220 mesh i.e. approximately 125-150 μm . Initially, no air is admitted through the inlet and plating is commenced at 2.7 amps per decimeter (25 amps per square foot) and then air is switched on for a period of 5 seconds. The boron nitride particles go into circulation and cascade over the assembly. Plating is then continued without the admissions of air for a period of approximately 40 minutes to secure the particles resting on the blade tips to the tips. It may be found that in some cases it is beneficial to have a further burst of 5 seconds of air after 20 minutes to ensure a uniform and maximum distribution of CBN particles over the blade tip surfaces.

The assembly is now removed from the CBN bath, is rinsed over the tank and is then rinsed in a static bath and finally rinsed thoroughly in running water. The surfaces being coated are then reactivated in a Woods nickel or 1% sulphuric acid bath and the fixture is replaced in the CoCrAlY bath. The motor is activated to rotate the assembly at 0.33 rpm and plating is continued for 7 hours at 1.075 amps per decimeter (10 amps per square foot) with continuous admission of air to maintain circulation of the solution and suspended CrAlY particles. This fills the spaces under and around the CBN particles with CoCrAlY to a depth which, as can be

seen in Figure 6, leaves the tips of the abrasive particles slightly proud of the surrounding CoCrAlY.

During the infilling process, the provide a matrix around the particles, the assembly may be rotated with a start-stop action. Thus the motor is controlled to produce a rotation of the assembly unidirectionally and at a speed of one rotation in 3 minutes with the rotation being intermittent with 10 second stop periods being interspersed with three second go periods. Optionally in addition the vibrator may be used. The vibrator is arranged to give a vibration at a frequency of 50 Hz with alternating periods of high intensity and low intensity vibration, the high intensity periods having a duration of 5 seconds and a peak acceleration of 10 g and the low intensity periods having a duration of 75 seconds with a peak acceleration of 2 g. The vibration and the rotation produce homogeneous infill and ensure that the CrAlY particles reach the areas shadowed by the CBN particles.

At the end of the infill stage the fixture is removed and the assembly is rinsed over the tank with demineralised water and then rinsed thoroughly in running water. The masking material is then removed and the assembly is taken out of the jig and degreased. After inspection the assembly is then heat treated from between 1/2 and 1 hour at 1090 plus or minus 10°C in vacuum or in 50-100 millibar partial pressure argon and fast gas quenched. The blades may then be aluminized by one of the well-known processes such as pack aluminizing.

One of the tips produced in the manner described is shown in section in Figure 6 and can be seen to comprise the body 80 of the blade, a binding coat 81 of MCrAlY of a thickness, in this example, of 25-50 μm , an anchoring coat 82 of MCrAlY of a thickness of 10-20 μm in which is anchored the bottom portions of the abrasive particles 83

of cubic boron nitride with a particle size of 125-150 μm , and an infill 84 of MCrAlY with a thickness of 70-110 μm .

5 Instead of particles of pure cubic boron nitride it
would be possible to use particles of this or another
abrasive which are coated with a material which will
protect them, for a time at least, from severe oxidation.
For example, it would be possible to use cubic boron
nitride particles which had been given a substantially
10 air-impermeable coating of aluminium oxide or an
intermetallic such as nickel aluminide.

Claims:

1. A method of producing abrasive tips on compressor or turbine rotor blades by electrolytic or electroless deposition, characterised in that at least part of the deposition process is conducted on the blade assembly on a compressor or turbine rotor disc.
2. A method as claimed in claim 1 in which the deposition process comprises producing a binding coat on the tips of the blade body by electrolytic or electroless deposition, the binding coat comprising MCrAlY where M is one or more of iron, nickel and cobalt, anchoring to the binding coat coarse particles of an abrasive material by composite electrolytic or electroless deposition from a bath of plating solution having the abrasive particles suspended therein, and then plating an infill around the abrasive particles.
3. A method as claimed in claim 2 in which the anchoring material is cobalt or nickel.
4. A method as claimed in claim 2 or claim 3 in which the anchoring material is MCrAlY where M is Ni or Co or Fe or two or all of these metals.
5. A method as claimed in claim 3 or claim 4 in which the thickness of the anchoring material is less than 30 μm .
6. A method as claimed in any of the claims 2 to 5 in which deposition of the infill material is followed by a heat treatment step applied to the assembly to homogenise the material of the layers other than the abrasive particles.

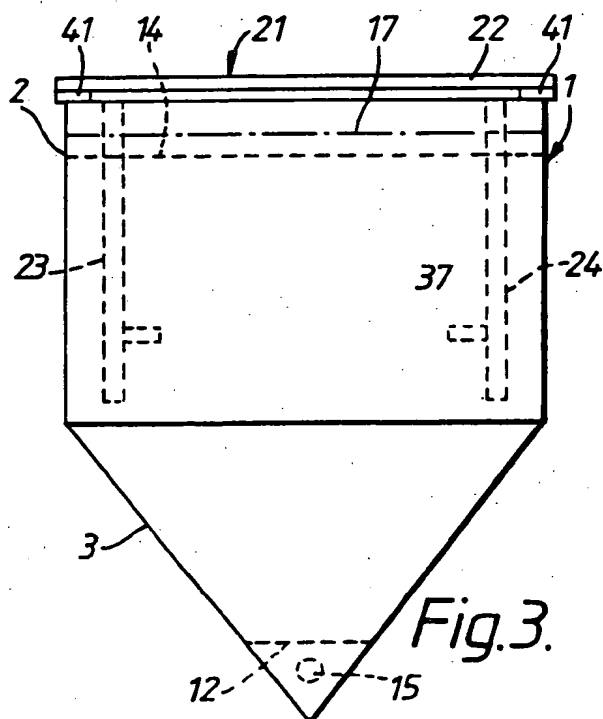
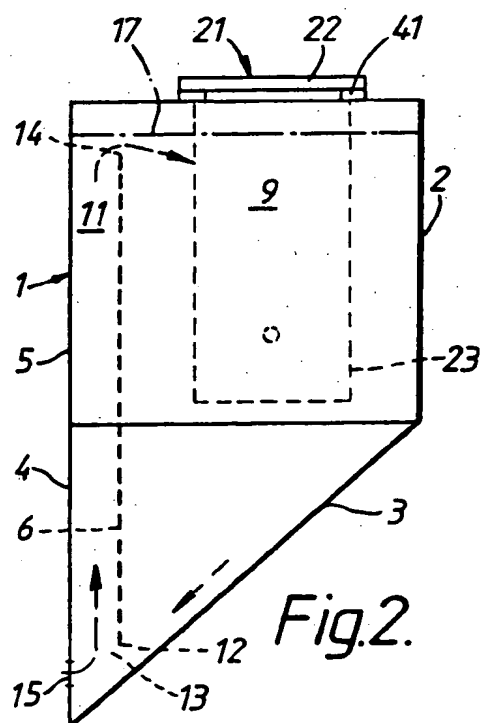
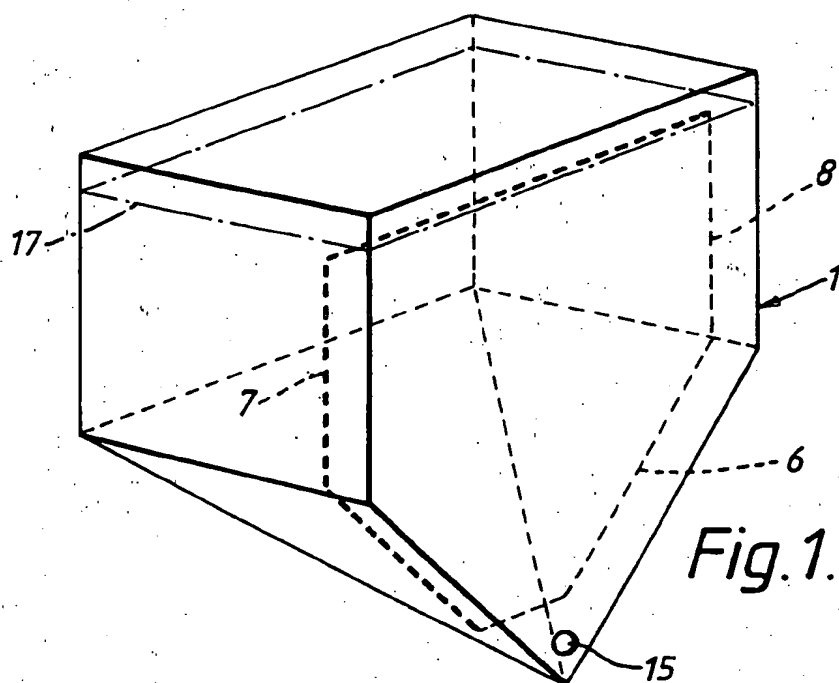
7. A method as claimed in claim 6 in which the heat treatment is followed by an aluminizing step to aluminize the blade tips.

5 8. A method as claimed in any of the preceding claims in which at least part of the deposition is accompanied by vibration of the assembly.

10 9. A method as claimed in claim 9 in which the vibration is in a vertical direction.

10. A method of producing abrasive tips on compressor or turbine rotor blades substantially as described herein with reference to the accompanying drawings.

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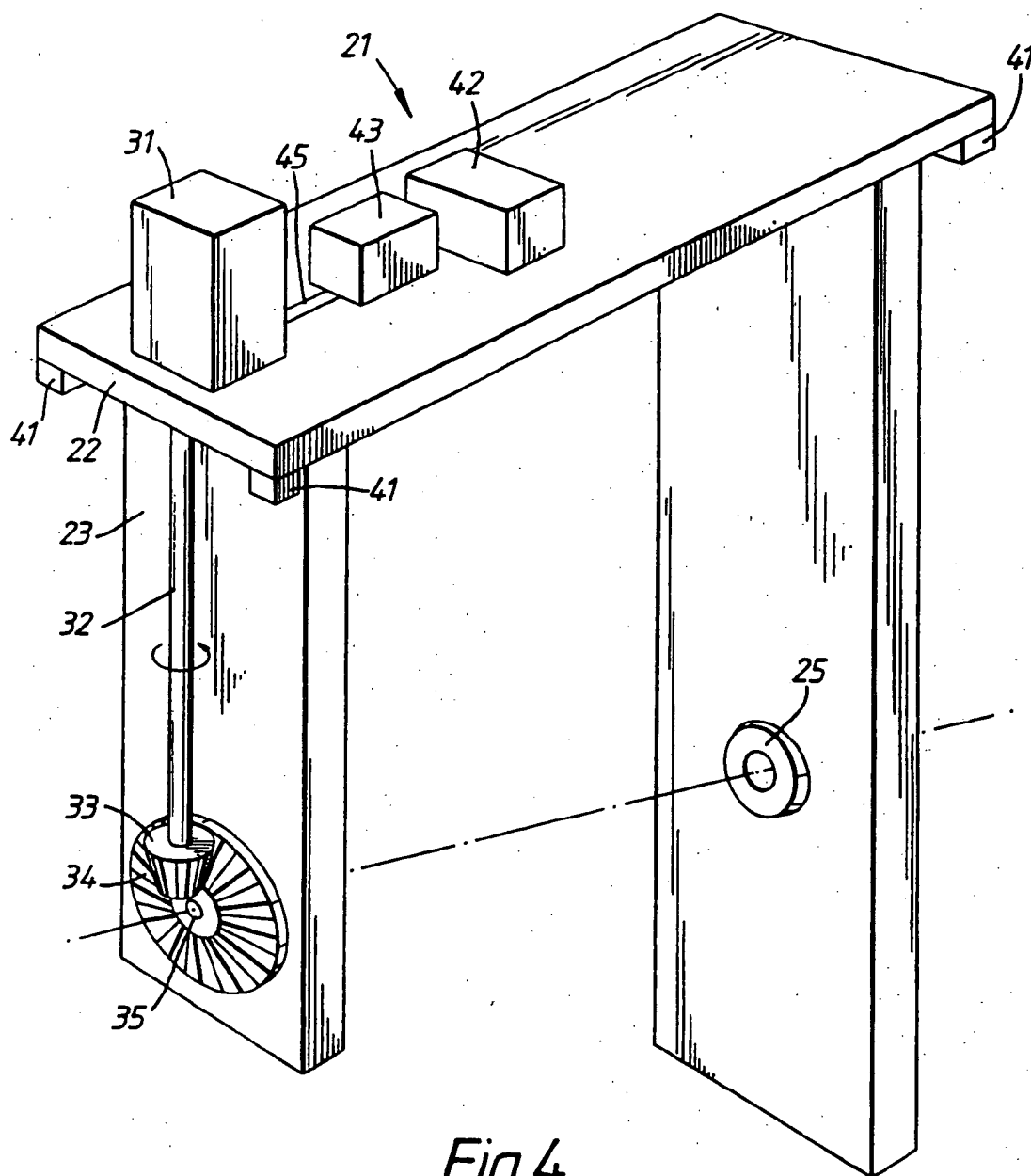


Fig.4

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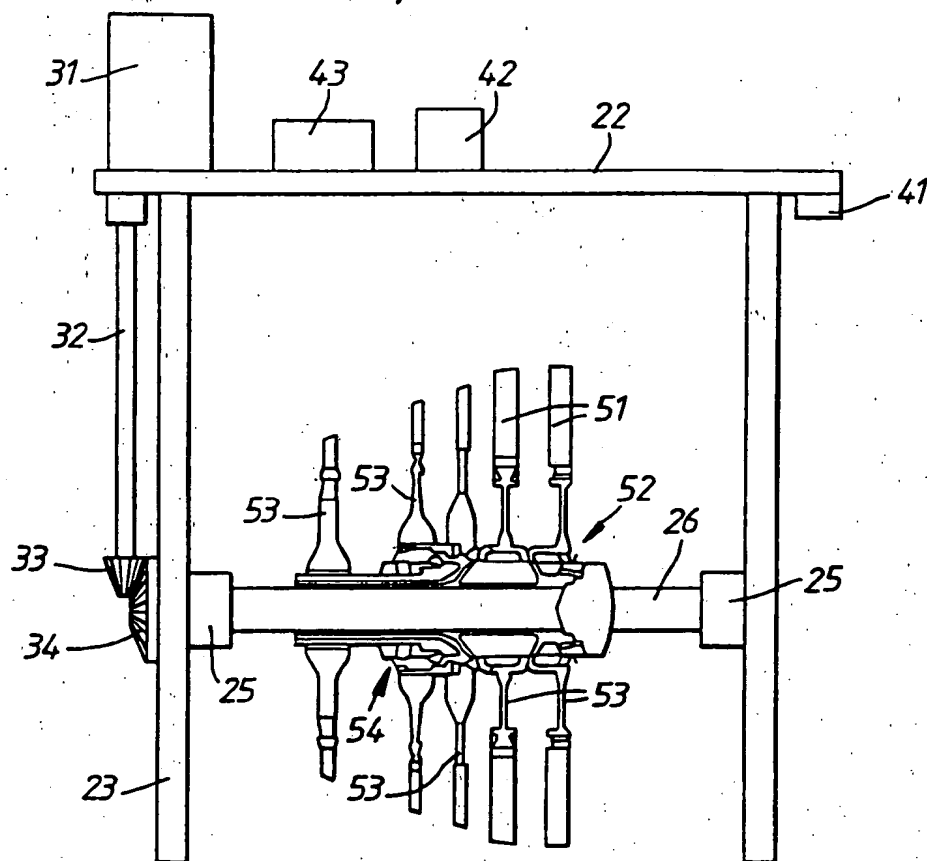


Fig. 5

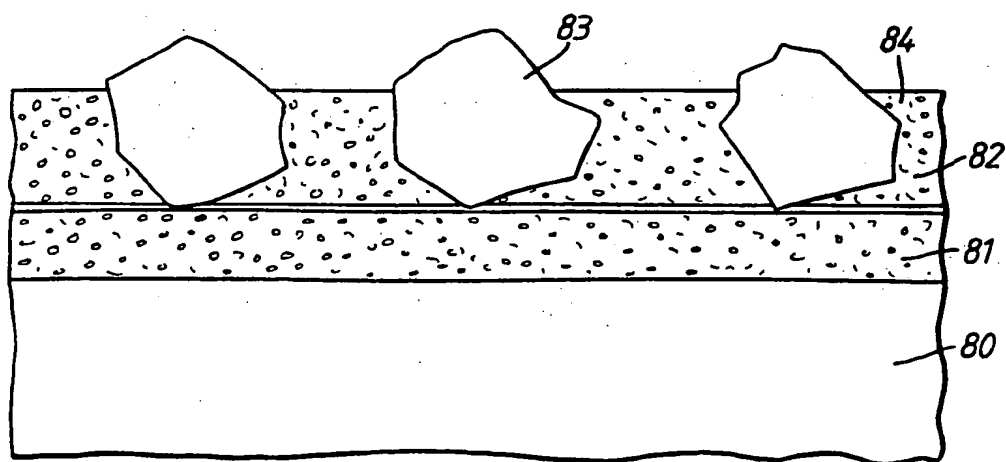


Fig. 6

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 94/00374

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 F01D5/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 F01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 241 506 (BAJ) 4 September 1991 cited in the application see the whole document ---	1-10
A	EP,A,0 355 051 (BAJ) 21 February 1990 cited in the application see figure 4 ---	1
A	GB,A,2 162 201 (GEC) 29 January 1986 see figure 3 ---	1
A	FR,A,2 649 125 (UTC) 4 January 1991 see abstract ---	1
A	US,A,4 584 081 (COULON) 22 April 1986 see abstract ---	1
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Patent family members are listed in annex.

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Date of the actual completion of the international search

9 May 1994

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 94/00374

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 345 977 (BLANC ET AL.) 24 August 1982 ---	1
A	EP,A,0 404 020 (REFURBISHED TURBINE COMPONENTS LTD.) 27 December 1990 see column 1, line 16 - line 41; figure 1 ---	1
A	GB,A,2 182 055 (BAJ) 7 May 1987 cited in the application ---	
A	GB,A,2 167 446 (BAJ) 29 May 1986 cited in the application -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 94/00374

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2241506	04-09-91	DE-D- 69100853	10-02-94
		DE-T- 69100853	21-04-94
		EP-A- 0443877	28-08-91
		ES-T- 2047373	16-02-94
		JP-A- 4218698	10-08-92
		US-A- 5076897	31-12-91
EP-A-0355051	21-02-90	GB-A, B 2221921	21-02-90
		GB-A, B 2254338	07-10-92
		JP-A- 2138497	28-05-90
		JP-B- 4071998	17-11-92
		US-A- 5037513	06-08-91
GB-A-2162201	29-01-86	US-A- 4608128	26-08-86
		CA-A- 1279030	15-01-91
		DE-A- 3525079	30-01-86
		FR-A- 2567916	24-01-86
		JP-B- 5021994	26-03-93
		JP-A- 61052390	15-03-86
		NL-A- 8502097	17-02-86
FR-A-2649125	04-01-91	US-A- 5074970	24-12-91
		DE-A, C 4021044	17-01-91
		GB-A, B 2234526	06-02-91
		JP-A- 3047996	28-02-91
US-A-4584081	22-04-86	FR-A- 2563540	31-10-85
		DE-A- 3564707	06-10-88
		EP-A, B 0165408	27-12-85
		JP-B- 5014030	24-02-93
		JP-A- 60234996	21-11-85
US-A-4345977	24-08-82	AT-T- 5267	15-11-83
		EP-A, B 0037033	07-10-81
		JP-A- 57019394	01-02-82
		US-A- 4279706	21-07-81
EP-A-0404020	27-12-90	AU-B- 638027	17-06-93
		AU-A- 5763190	03-01-91
		DE-D- 69006268	10-03-94

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 94/00374

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0404020		DE-T- 69006268	05-05-94
		GB-A, B 2233261	09-01-91
		JP-A- 3033405	13-02-91
		US-A- 5149073	22-09-92
		US-A- 5235745	17-08-93
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GB-A-2182055	07-05-87	NONE	
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GB-A-2167446	29-05-86	BE-A- 903377	04-04-86
		CA-A- 1268139	24-04-90
		DE-A- 3535548	17-04-86
		FR-A- 2571386	11-04-86
		JP-C- 1627755	28-11-91
		JP-B- 2053520	16-11-90
		JP-A- 61179900	12-08-86
		NL-A- 8502724	01-05-86
		US-A- 4789441	06-12-88
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